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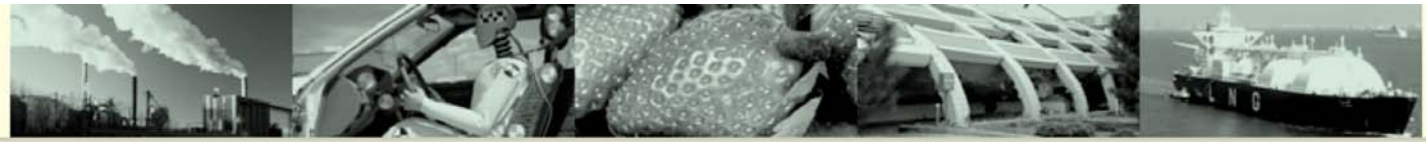

From Lithium Plating to Lithium – Ion Cell Thermal Runaway

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November 19, 2009

Who We Are

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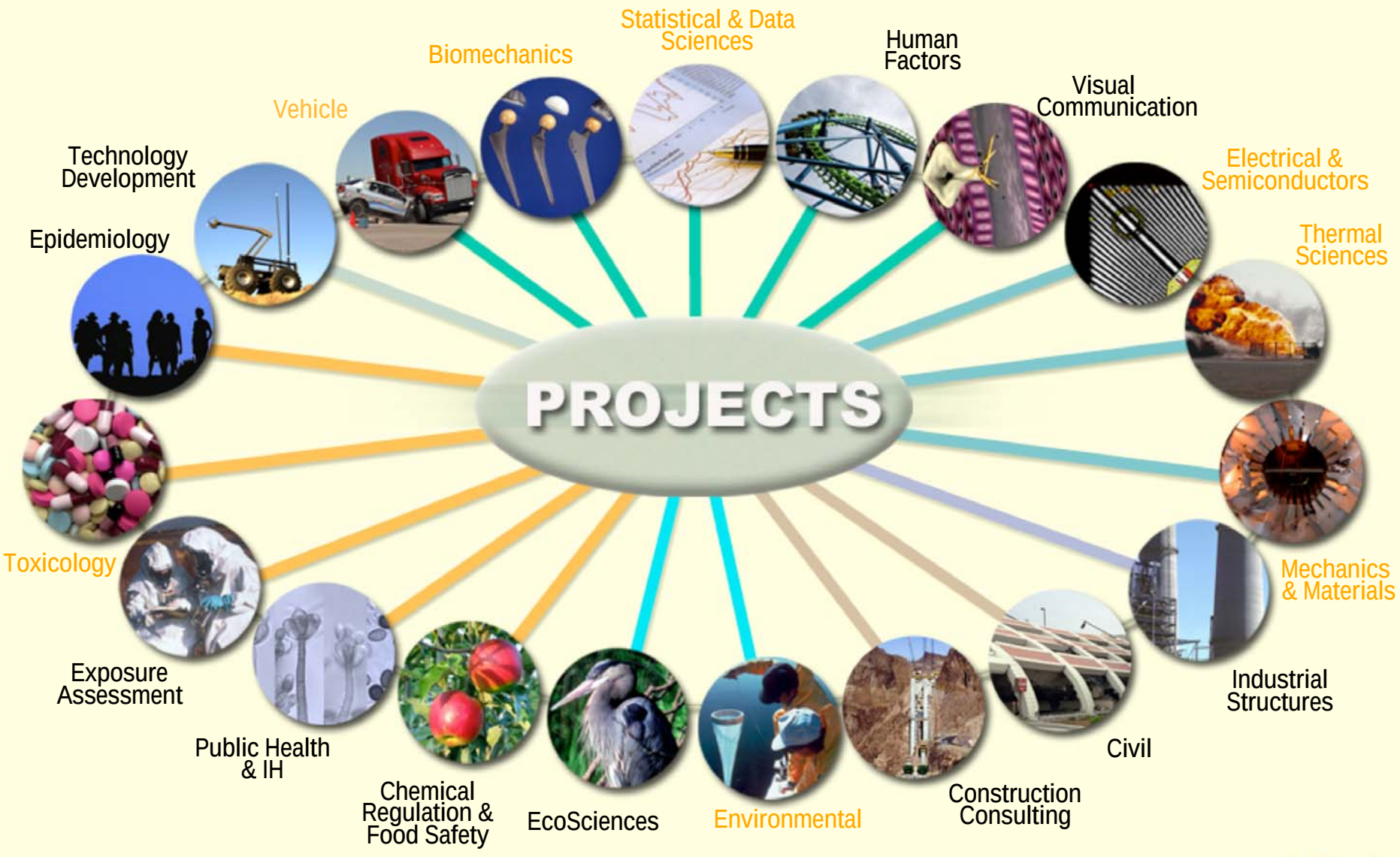
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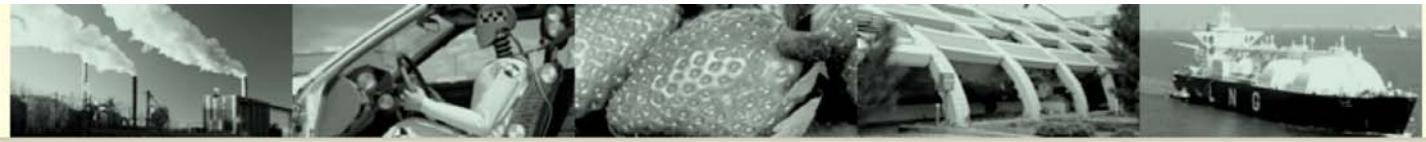


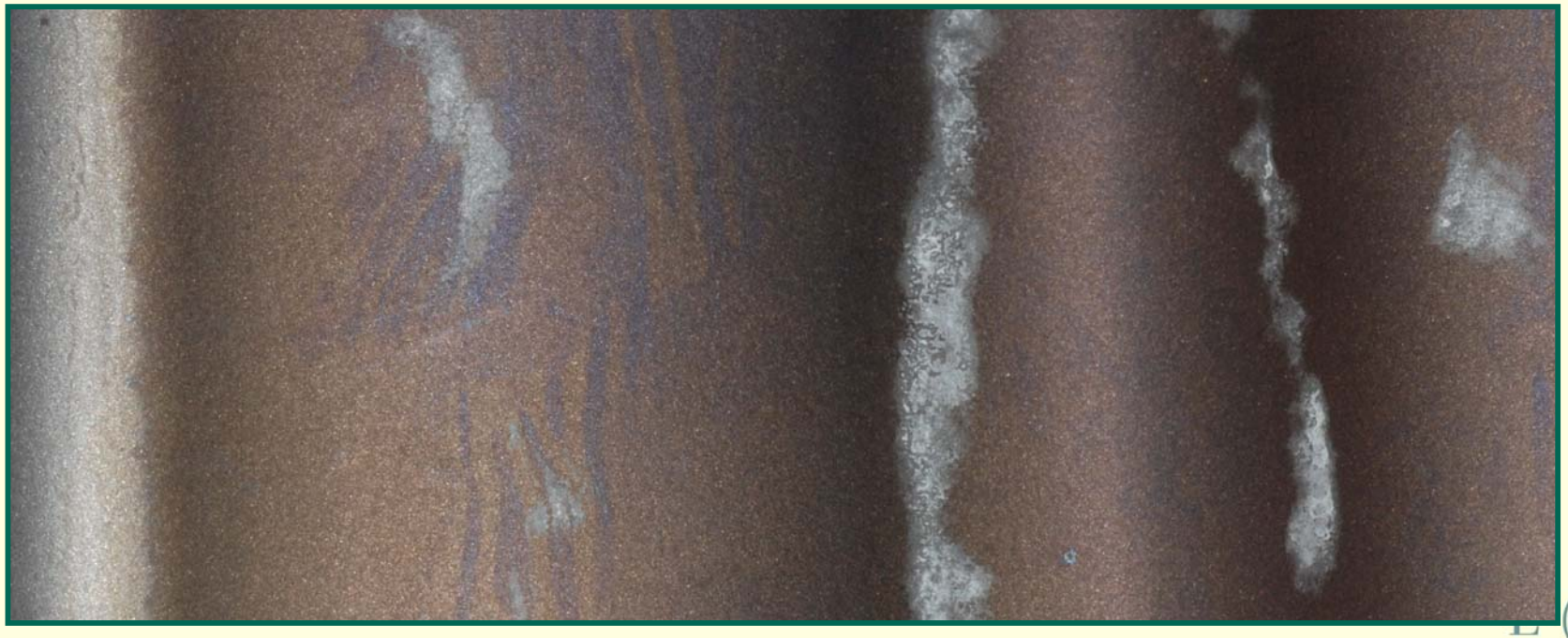
Battery Support Services

- Cell design review & assessment
- Pack design review & assessment
  - Electronics & BMU consulting
  - Thermal management
  - Structural evaluation
- Pre-compliance testing (UN, UL, BAJ, vendor specific)
- Verification & safety evaluation testing
- Failure analysis & corrective action recommendations
- Manufacturing auditing
- Recall support

- CTIA Program
- Cell cross-section analysis
- CT scanning
- Micro-reference electrode testing
- Accelerating rate calorimetry (ARC)
- Thermal analysis of materials (TGA/DSC)
- Materials characterization (SEM-EDS, XRD, FTIR, GC-MS)
- Custom abuse and service testing
- Fundamental electrochemical analysis
- Accelerated life testing and prediction
- Gas analysis
- Vent and CID activation

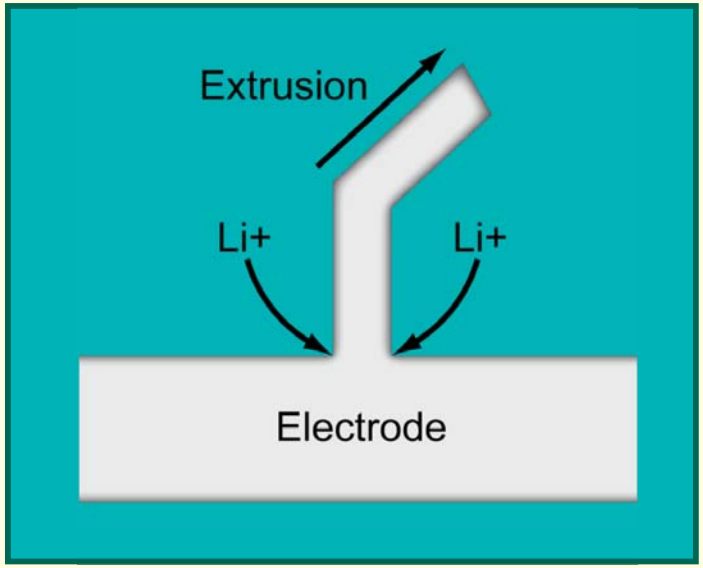
What is Lithium Plating?

- Lithium ions deposit as metallic lithium on the negative electrode surface during charging instead of intercalating into graphite



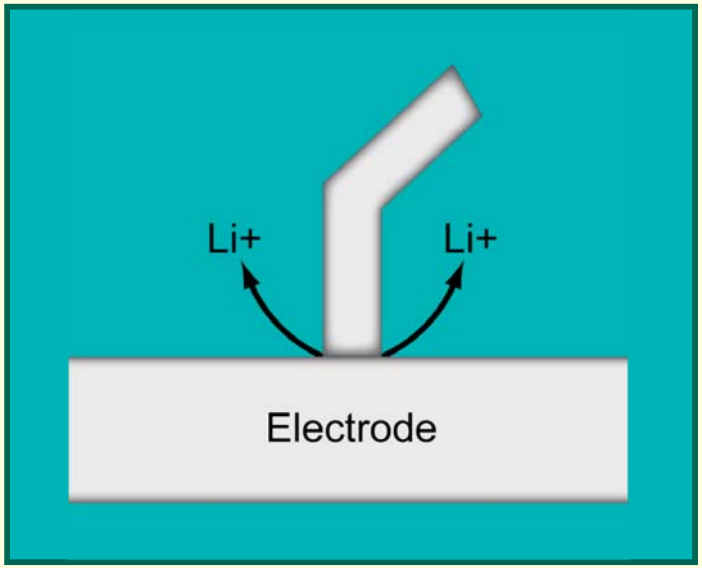
How Exactly Does Lithium Deposit?

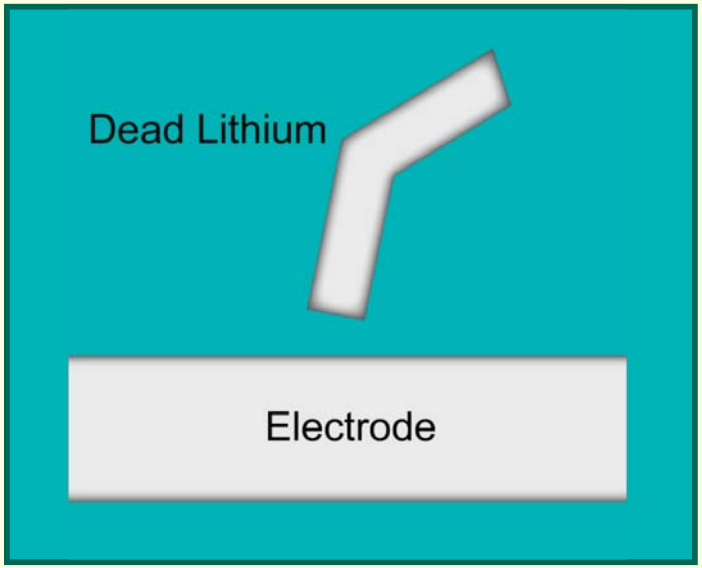
- Current research suggests
  - Initially, lithium dendrites grow as an extrusion process – lithium deposits at the base of the dendrite and pushes the tip through a weak spot in the SEI
  - In later stages, lithium will deposit at dendrite tips and kinks



Does Plated Lithium Re-Dissolve During Discharge?

- A number of researchers have observed the formation of "dead lithium"
  - On discharge, some lithium dissolves from the dendrite tip and body, but the rate of dissolution at the dendrite base can be higher resulting in lithium separation from the cell base





Does Plated Lithium Re-Dissolve During Discharge?

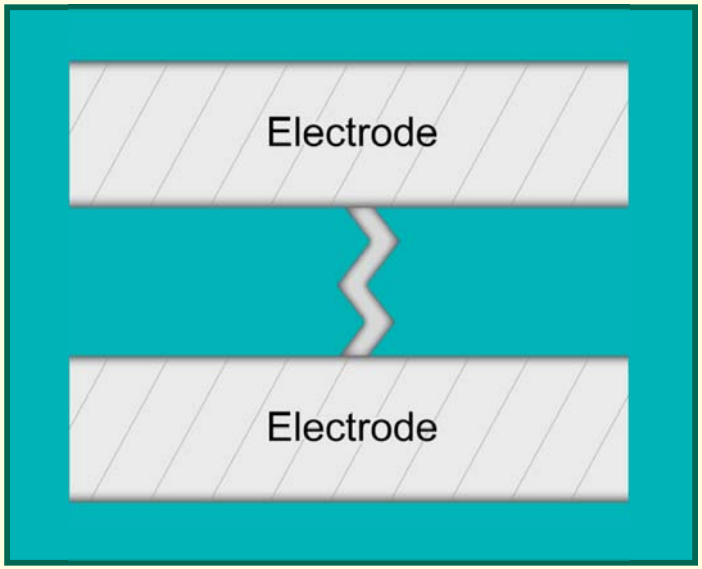
- Evidence of residual, plated lithium can be found in discharged cells
- $Li\ (s) + H_2O \rightarrow LiOH + \frac{1}{2}\ H_2(g)$

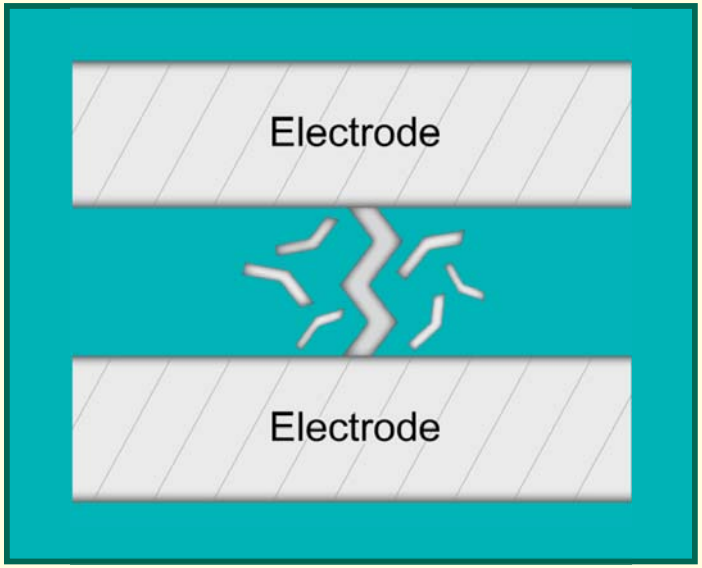
What Happens to the Plated Lithium?

- Re-dissolution during discharge
- Formation of dead lithium deposits
- Reaction with electrolyte to form SEI
  - Reduces cell rate capability – impedance increases
  - Enhances likelihood of subsequent lithium plating
  - Enhances likelihood of localized over-discharge

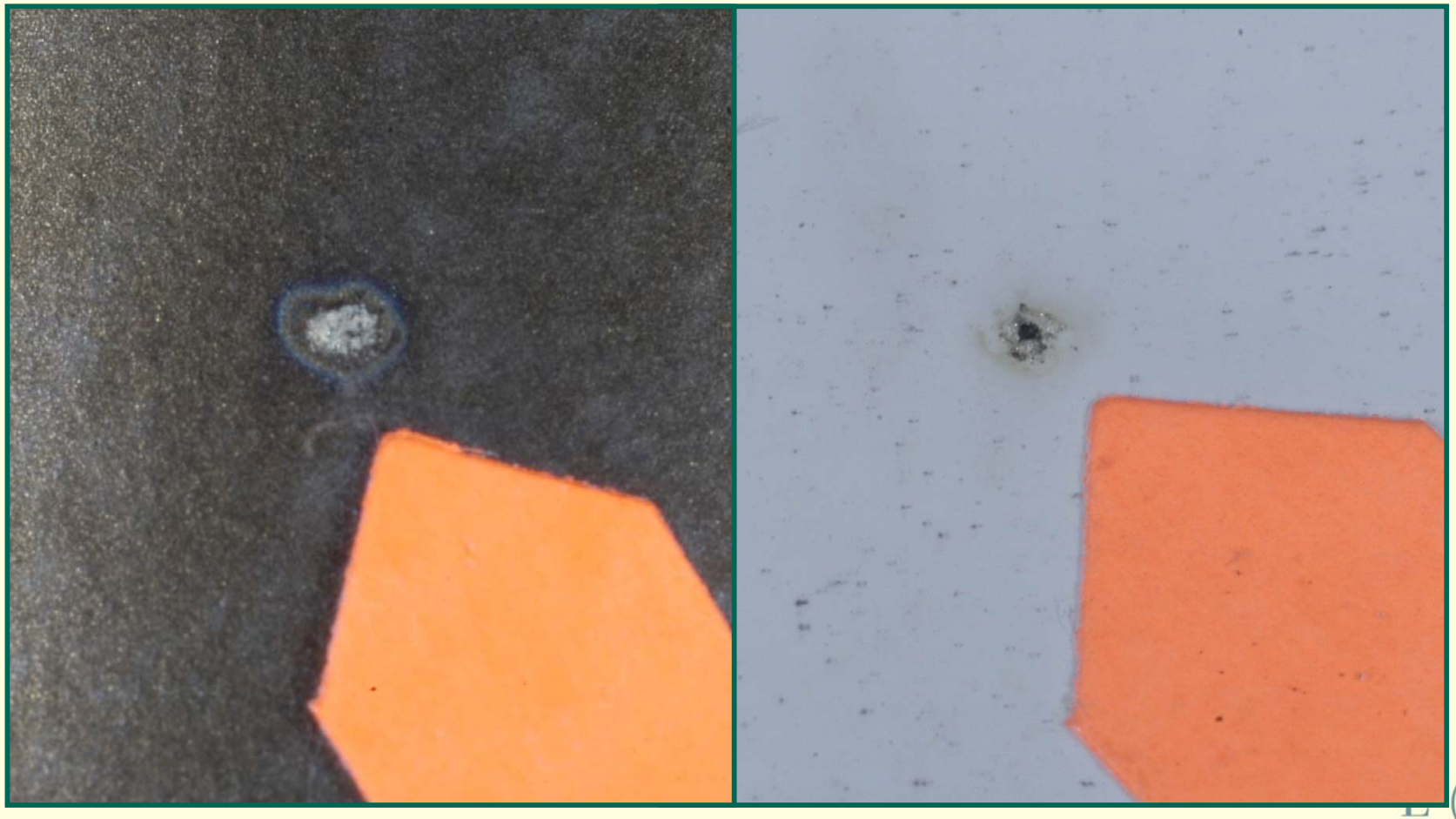
Negative Effects of Plated Lithium

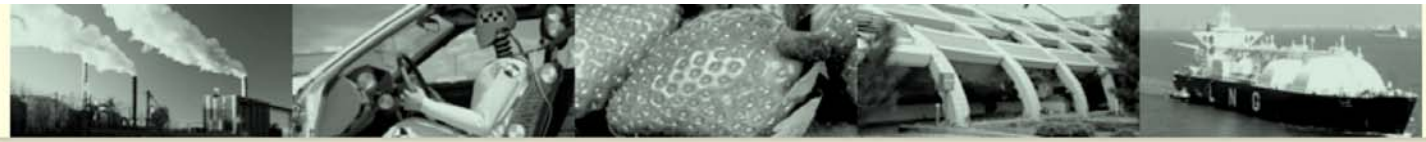
- Irreversible Loss of Lithium
- Dendrites can cause shorting within the cell
- A mat of dendrites and dead lithium can increase the likelihood that a minor short will lead to cell thermal runaway





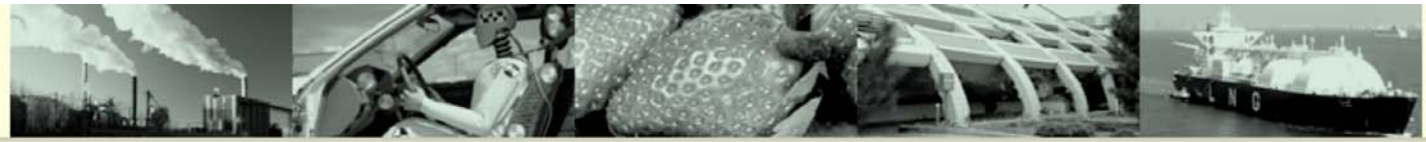
Plated Lithium & Micro-short





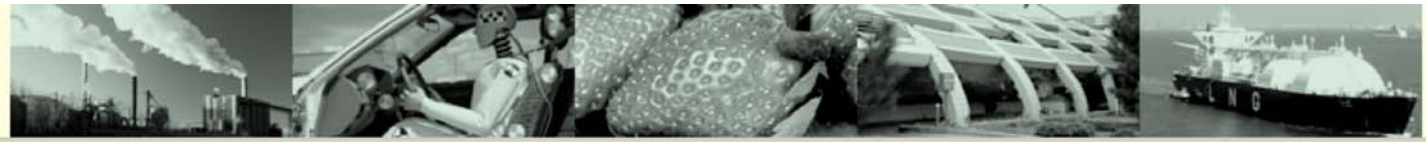
Fine Metal Particle Ignition & Combustion

- Metal burning extensively examined in combustion literature
  - Metal (Aluminum) powder in solid rocket propellants
    - Metal particles randomly mixed with oxidizer and binder (polymer)
    - 10 to 40 μm particles
    - Propellant is stable at low temperatures
    - Metal is added to increase specific impulse: higher combustion temperatures, faster energy release once propellant is ignited
  - Self- Propagating High Temperature Combustion Synthesis (SHS) reactions of powder compacted materials
    - Intimate mixing of metal and oxidizer
    - High reaction temperatures achieved due to metal oxidation – e.g. thermite reaction



Fine Metal Particle Ignition & Combustion

- Solid / liquid fuels are “easier” (lower energy for ignition) to ignite if finely divided and intimately mixed with oxidizer
  - Approach ideal case of a vapor phase pre-mixture
  - For example:
    - Atomization of diesel fuel in engines
    - Dust explosions (grain silos), metal shaving fires
- Metal combustion is typically very energetic
  - Large enthalpy of reaction
  - High flame temperatures relative to typical combustibles

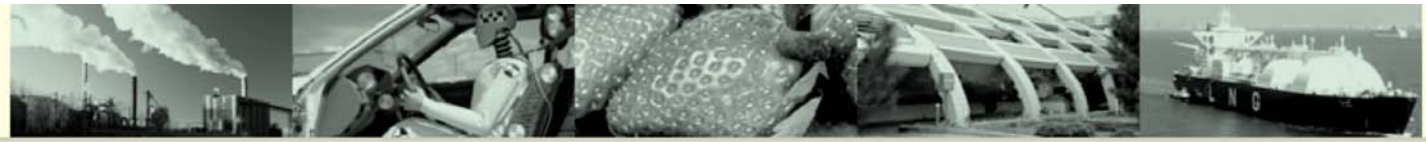


Lithium Ignition Temperatures

- Melting point of lithium: ~180 C
- Measured ignition temperatures of lithium are at or above the melting point of lithium
  - Melting disrupts protective oxide coatings allowing high reaction rates
- Water (or OH-) likely reduces ignition temperature significantly
  - Lithium reacts significantly with water below its melting point
  - Appears to have a catalytic effect on lithium reaction
  - Uncertain / broad ranges in ignition temperatures suggest that moisture content in gas was not controlled

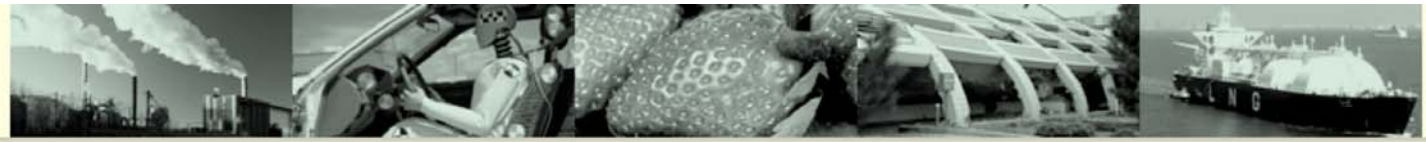
Oxidizing Atmosphere	Measured Ignition Temperatures*
Oxygen (Dry Oxygen)	190-630 C (607-630 C)
Air	180 – 640 C
CO_2	330 C
N_2 (Dry N_2)	170-450 (420-600 C)
Ar / N_2 / CO_2 mixtures	310 – 433 C
Carbon	> 800 C
Paraffin vapor (C-H compounds)	~ 200 C

*Data from Lithium Combustion Review by Rhein



Lithium Ignition Temperatures

- ARC tests of primary cells show sharp exotherms near lithium melting temperature:
  - 172 C lithium thionyl chloride cell
  - 197 C lithium iron disulfide cell
  - 157 C lithium manganese dioxide cell
- DSC tests of lithium with:
  - Dry electrolytes show exotherm at ~ 180 C
  - Electrolyte + 1% water shows exotherm at ~ 140 C
- ARC tests of lithium–ion cells with plated lithium:
  - Exhibit no appreciable change in reactivity below lithium melting temperature
  - Exhibit a sharp exotherm near 150 C
    - Similar to a lithium manganese dioxide cell
    - Near lithium melting temperature
    - Lithium-ion cell electrolyte will include compounds (contaminants or decomposed electrolyte) that readily form OH- groups, likely leading to catalysis of lithium reaction



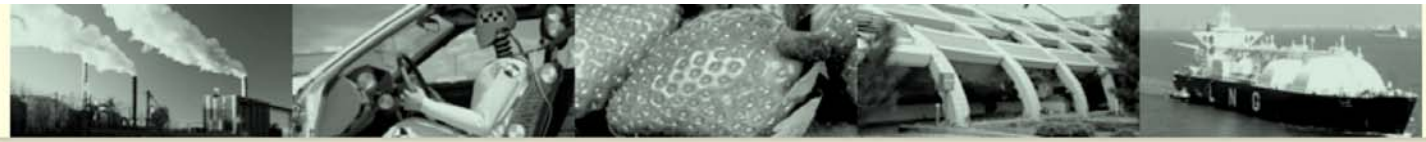
Lithium Flame Temperatures

- Form of combustion reaction will depend upon the reactants and final products (Glassman's criteria)
  - Vapor phase (homogeneous) combustion in oxidizing environments where vaporization / dissociation temperature of the oxide product exceeds boiling point of lithium metal (~1342 C)
  - Surface phase (heterogeneous) combustion where vaporization / dissociation temperature of the oxide product is lower than boiling point of lithium metal
- Flame temperatures will be
  - Limited by the dissociation/volatilization temperature of the metal oxide
  - Reduced by presence of diluents

Possible Product	Vaporization / Dissociation Temperature
Li_20	2563 C
LiF	1676 C
LiCl	1382 C
Li_2S	1372 C
Li_2CO_3	1310 C
LiOH	924 C
LiH	850 C
Li_3N	813 C

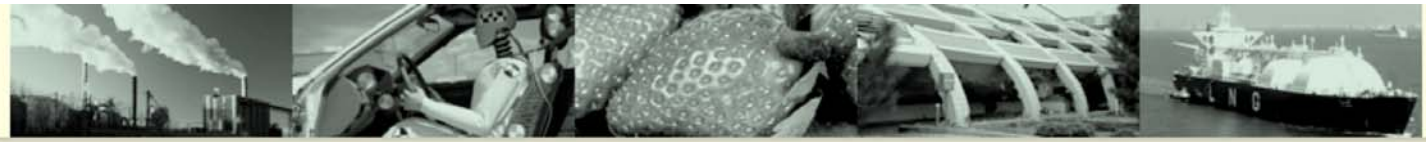
Vapor Phase Burning

Surface Burning



Lithium Combustion Temperatures

Reactants	Products	Flame Temperature or Maximum Measured Temperatures
Li / O_2	Li_20	2300 - 2600 C Vapor phase burning
Li / 21% O_2 / Ar	Li_20	1800 C (0.07 atm) Vapor phase burning
Li / Dry Air	Li_20, Li_3N, Li_2CO_3	1260-1350 C Vapor phase burning
Li / Moist Air	Li_20 , Li_3N, Li_2CO_3 , LiOH	1150 C Vapor phase burning
Li / CO_2	Li_20 , Li_2CO_3 , C, Li_2C_2	> 1800 C Vapor phase burning
Li / CO_2 / N_2 / Ar	Li_20 , Li_2CO_3 , Li_3N, C, Li_2C_2, CO, C	Vapor phase burning
Li / N_2 (dry)	Li_3N	820-830 C Surface burning
Li / C	Li_2C_2	Surface burning
Li / C_2H_4	LiH, Li_2C_2	Surface burning

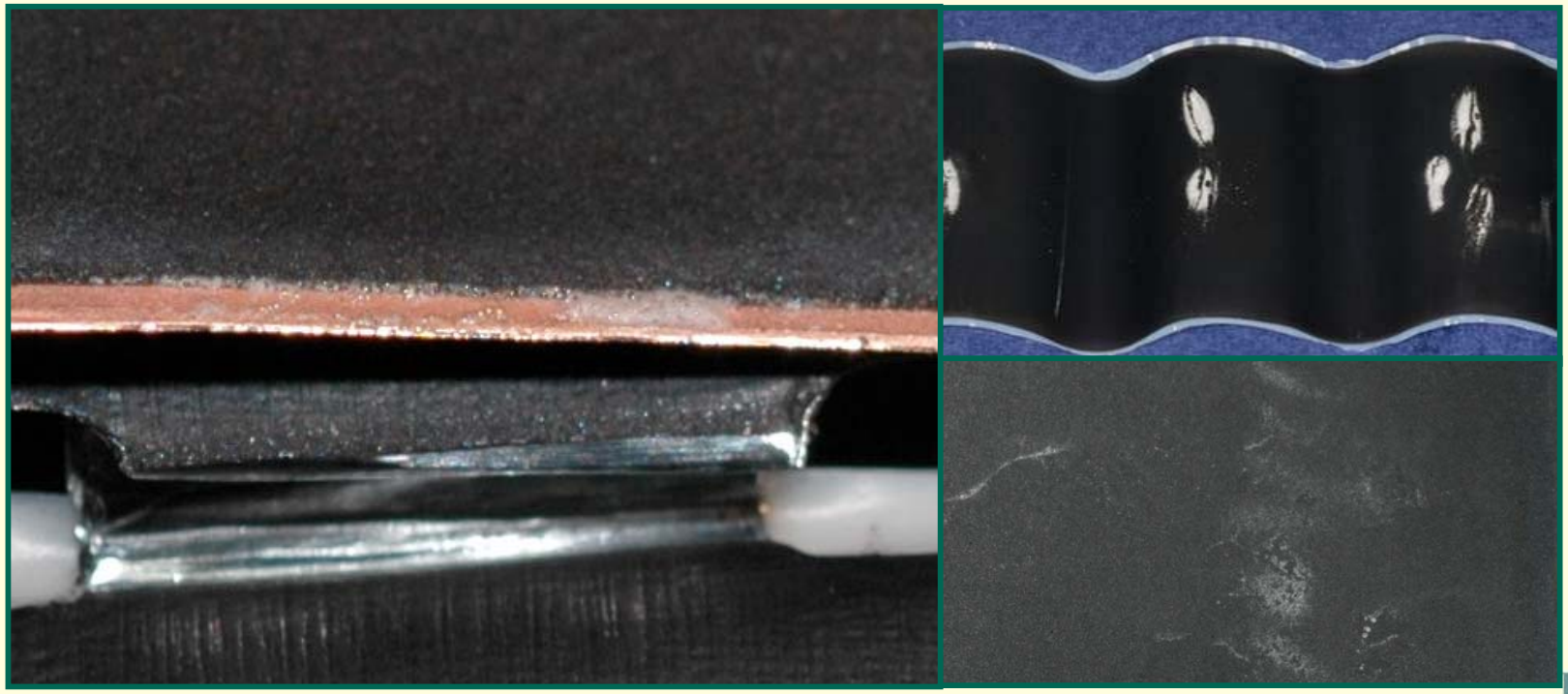


Lithium Combustion Temperatures

- High temperature reaction product distribution of metallic lithium within a lithium-ion cell has not been determined but expect that this can produce a high heat release rate
  - Typical electrolytes include molecules with carbonate groups (OCO_2-)
  - Postulated anode/ electrolyte decomposition products include: Li_20, Li_2CO, LiOH
- It has not been determined, but if sufficient heat is released by combustion of one dendrite to ignite surrounding dead lithium, thermal runaway may become more likely

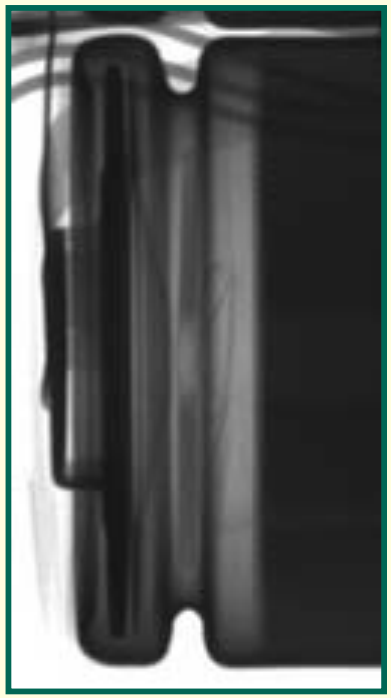
Lithium Plating in Commercial Cells

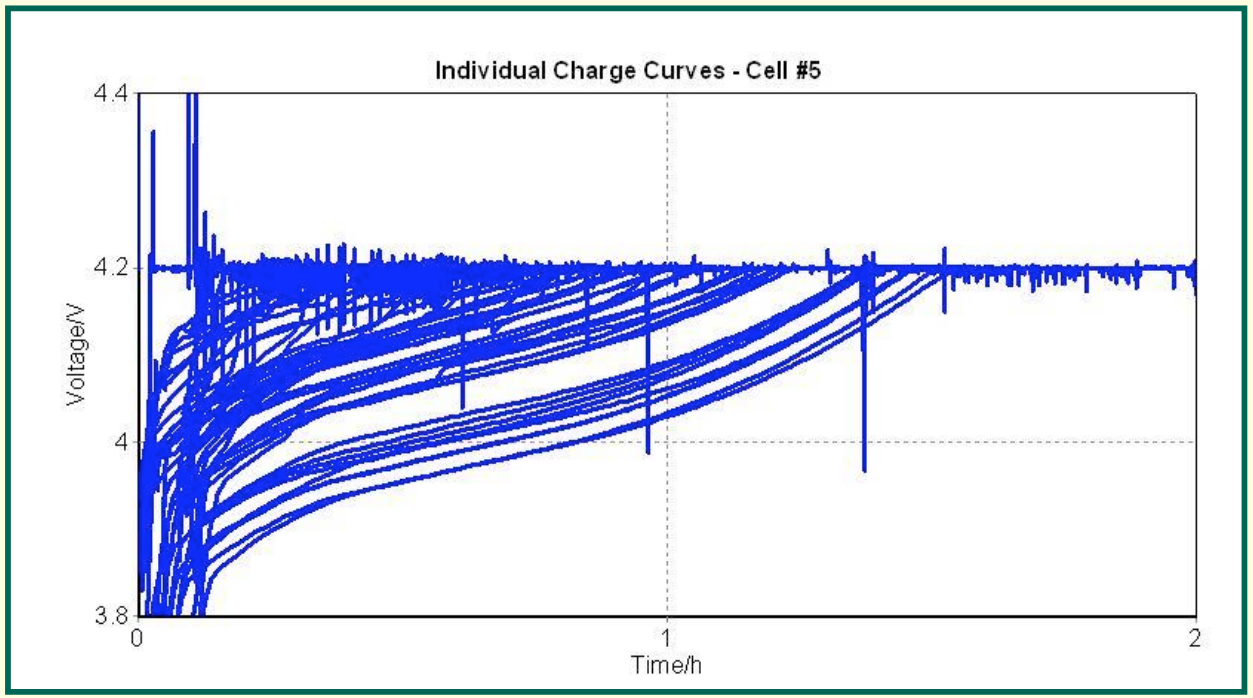
- Lithium plating can occur in commercial cells due to a variety of cell manufacturing problems, as well as usage and aging scenarios



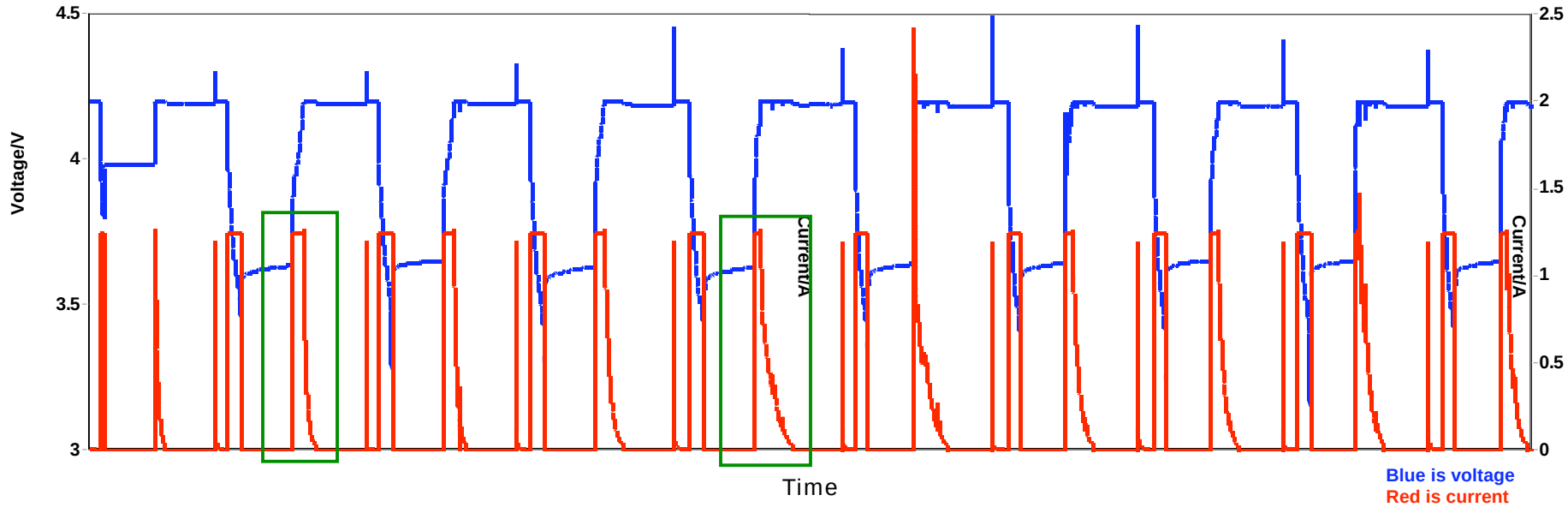
Behavior of a Cell with Lithium Plating

- Dendrite shorting has been observed in test cells by other researchers
- Dendrite shorting has been observed by Exponent in commercial cells



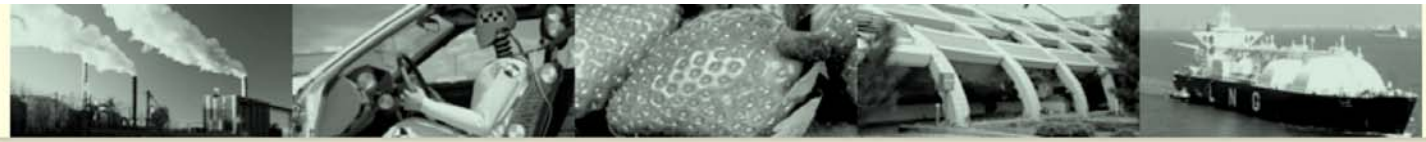


Behavior of a Cell with Lithium Plating



Normal Taper Current Profile

Extended Taper Current Profile



Can Existing Dead Lithium Be Oxidized Away?

- Possibly - no known studies available
- Oxidation rate of dead lithium
  - Likely to be controlled by diffusion rate of reactants through SEI layer
    - Thickness / permeability of SEI
    - Reactant species distribution surrounding the dead lithium
    - Temperature
  - Should not be significantly affected by cycling – although this could have a secondary roll in affecting reactant species distribution
  - Likely to vary with cell model

Can Existing Dead Lithium Be Oxidized Away?

- Could be studied in commercial cells
  - Cause plating through severe cycling regime in commercial cells, particularly after aging
  - Subject cells to various conditioning regimes such as
    - Elevated temperatures at full charge
    - Elevated temperature at low charge
  - Examine cells for evidence of lithium metal and lithium metal oxidation
    - Visual exam
    - ARC
    - SEM / EDS
    - XRD

Conclusions

- Lithium plating can have many deleterious effects on cells
- Lithium plating can enhance the likelihood of cell thermal runaway due to the formation of a mat of dead lithium in proximity to an area of dendrite formation
- Localized lithium plating and shorting behavior consistent with dendrite formation has been observed in commercial cells
- Possible that dead lithium, once formed could be eliminated through oxidation

Acknowledgements

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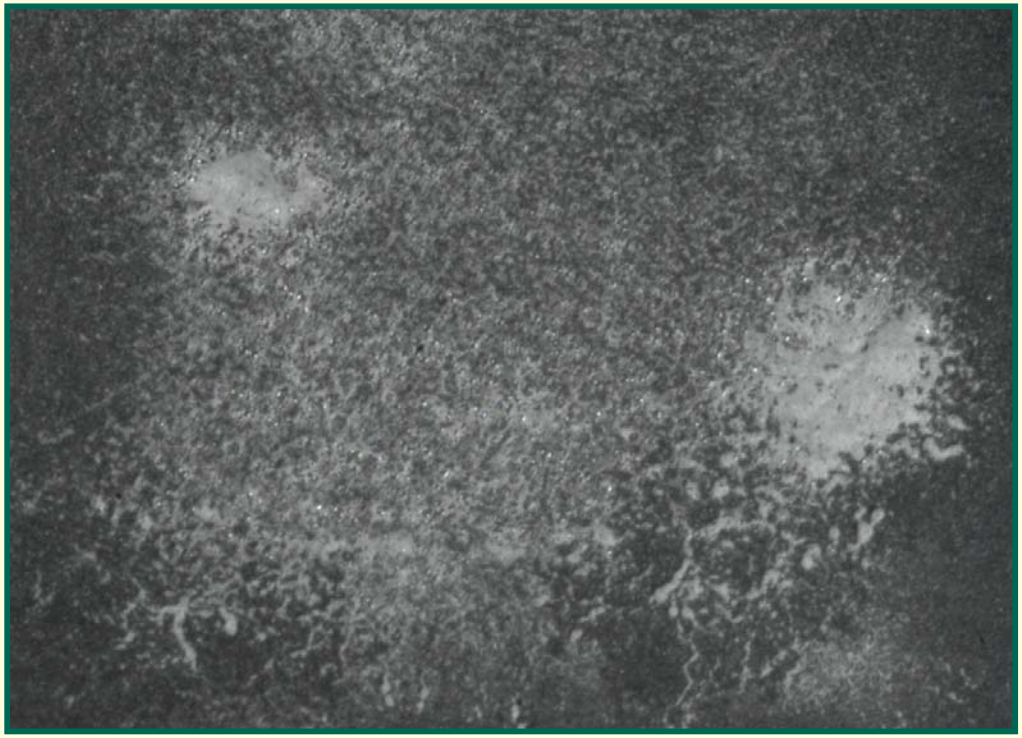

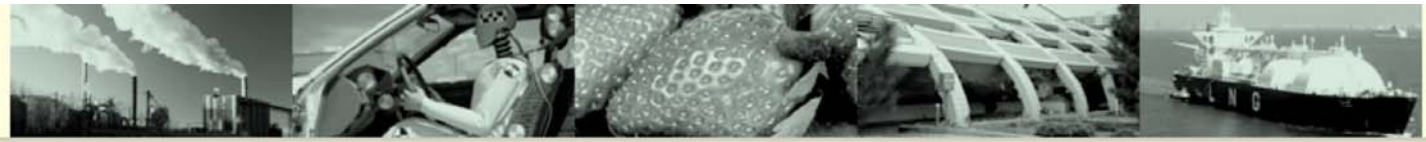

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Questions?